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KINETICS AND MECHANISM OF THE THERMAL DECOMPOSITION OF HYDRAZINIUM SALTS

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U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	*А а*	A, a	Р р	*Р р*	R, r
Б б	*Б б*	B, b	С с	*С с*	S, s
В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
З з	*З з*	Z, z	Ч ч	*Ч ч*	Ch, ch
И и	*И и*	I, i	Ш ш	*Ш ш*	Sh, sh
Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

FOLLOWING ARE THE CORRESPONDING RUSSIAN AND ENGLISH

DESIGNATIONS OF THE TRIGONOMETRIC FUNCTIONS

Russian	English
sin	sin
cos	cos
tg	tan
ctg	cot
sec	sec
cosec	csc
sh	sinh
ch	cosh
th	tanh
cth	coth
sch	sech
csch	csch
arc sin	$\sin^{-1}$
arc cos	$\cos^{-1}$
arc tg	$\tan^{-1}$
arc ctg	$\cot^{-1}$
arc sec	$\sec^{-1}$
arc cosec	$\csc^{-1}$
arc sh	$\sinh^{-1}$
arc ch	$\cosh^{-1}$
arc th	$\tanh^{-1}$
arc cth	$\coth^{-1}$
arc sch	$\sech^{-1}$
arc csch	$\csch^{-1}$

———

|	
rot	curl
lg	log

KINETICS AND MECHANISM OF THE
THERMAL DECOMPOSITION OF HYDRAZINIUM*
SALTS

Yu. I. Rubtsov

(Chernogolovka)

At the First Symposium on Combustion and Explosion the results
of an investigation of the thermal decomposition of hydrazinium
nitrate were presented, [1, 2]. It was shown that the reaction
takes place through dissociation of the salt in the liquid phase
into hydrazine and nitric acid, while the reaction rate is deter-
mined by the hydrazine decomposition rate.

To explain the applicability of this mechanism to other
hydrazinium salts we investigated the kinetics of the thermal
decomposition of hydrazinium chloride, iodide, and azide and their
mixtures with hydrazine and other additives. The reaction rate
was studied with respect to the rate of heat release in a
microcalorimeter [3] in sealed glass ampoules having no cold
parts. It was found that the first stage is common to all com-
pounds - the equilibrium dissociation of the salt into hydrazine
and the corresponding acid in the liquid phase:

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*Translator's Note: In the original Russian article and in this
translation, hydrazine salts are referenced as hydrazinium salts
because of the pertinency of the hydrazino radical ($N_2H_5^+$).

$$(N_2H_5X)_{liq} \rightleftarrows (N_2H_4)_{liq} + (HX)_{liq.} \qquad (1)$$
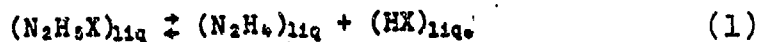
The hydrazine which was formed partially produces a complex with a hydrazinium ion:

$$(N_2H_4)_{liq} + (N_2H_5^+)_{liq} \rightleftarrows (N_4H_9^+)_{liq.} \qquad (2)$$

The existence of such complexes was shown from a study of the phase diagrams of the systems N_2H_4-$N_2H_5NO_3$ and N_2H_4-N_2H_5Cl and measurement of the equilibrium pressure of hydrazine over the system N_2H_4-N_2H_5Cl. The corresponding complex salts melt congruently at 3°C ($N_2H_5NO_3 \cdot N_2H_4$) and 36°C ($N_2H_5Cl \cdot N_2H_4$).

Further transformations of the dissociation products occur in various ways depending on the composition of the acid formed during dissociation of the salt. The limiting stage for hydrazinium nitrate and chloride is decomposition of the $N_2H_4 \cdot N_2H_5^+$ complex. This was confirmed during an investigation of the thermal decomposition in the systems N_2H_4-$N_2H_5NO_3$ and N_2H_4-N_2H_5Cl. The reaction rate

$$\frac{d[N_4H_9^+]}{dt} = k[N_2H_5^+] \cdot [N_2H_4]$$

rate constant k has the same value for both salts. Using the initial reaction rates in pure salts and the values of k, we can calculate the equilibrium concentration of hydrazine in the salt melt. For $N_2H_5NO_3$, for all practical purposes, the concentration is independent of temperature, and amounts to $\sim$0.2 mole/l. With the decomposition of N_2H_5Cl the initial stage of the reaction is somewhat distorted because of the parallel interaction of N_2H_5Cl with HCl.

In purer form, such interaction can be observed during the thermal decomposition of hydrazinium iodide. The stability of N_2H_5I is substantially lower; equal initial decomposition rates are observed at temperatures 100°C lower than in N_2H_5Cl and $N_2H_5NO_3$.

Most significant is the effect of hydrazine, which sharply reduces the reaction rate: upon its introduction into N_2H_5Cl and $N_2H_5NO_3$ the rate increased. The higher decomposition rate of N_2H_5I is associated with the interaction of the hydrogen iodide formed as in reaction (1) with the original salt, leading to a reduction of the hydrazine to ammonia:

$$N_2H_5I + HI \rightarrow 2NH_3 + I_2. \qquad (3)$$

The iodine quickly oxidizes hydrazine to nitrogen; the process goes totally according to the equation

$$3N_2H_5I = 3NH_4I + NH_3 + N_2. \qquad (4)$$
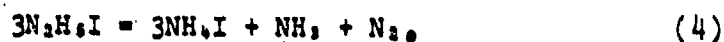
The decomposition rate constant of the complex $N_2H_4 \cdot N_2H_5^+$ is small at such temperatures and its contribution to this reaction can be disregarded. Additives which raise the acidity of a system, e.g., $N_2H_6Cl_2$, increase the thermal decomposition rate in accordance with the proposed mechanism.

We can assume that all hydrazinium salts formed by acids with well-pronounced reduction properties will also decompose, and their thermal stability will be significantly lower. The thermal decomposition of hydrazinium azide can serve to confirm this. Hydrazoic acid can reduce hydrazine to ammonia:

$$N_2H_5N_3 + HN_3 \rightarrow 2NH_3 + 3N_2. \qquad (5)$$
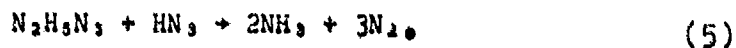
The distinction from hydrogen iodide is that the nitrogen formed cannot oxidize hydrazine as iodine can; therefore the hydrazine is a product of the reaction and accumulates in the system. In addition, HN_3 is far more volatile, and at 140-170°C most of it is in the gaseous phase. This leads to higher stability of hydrazinium azide. Since the reaction proceeds at higher temperatures and hydrazine accumulates in the system, which leads to an increase in concentration of the complexes $N_2H_4 \cdot N_2H_5^+$, the contribution of their thermal decomposition is essential to the total reaction.

Of the hydrazinium salts, in the literature there are data on the kinetics of decomposition only for $N_2H_6(ClO_4)_2$, $N_2H_5ClO_4$, and $N_2H_5ClO_4 \cdot 0.5H_2O$ [4-6]. A comparison of these works with the data derived above shows that the stability of $N_2H_5ClO_4$ is much lower than that of the nitrate or chloride, and approximates the stability of N_2H_5I; consequently, the decomposition of the complex $N_2H_4 \cdot N_2H_5^+$ is not a limiting stage. The mechanism of decomposition through perchloric acid, proposed in [6], cannot be accepted: hydrazinium diperchlorate, at the beginning of the reaction, decomposes more slowly than the perchlorate, but it should have decomposed much quicker; the equilibrium pressure of $HClO_4$ over it is 7-8 orders higher. When decomposition is limited, $HClO_4$, NH_4ClO_4, and $N_2H_5ClO_4$ should decompose at similar rates, since the basicity constants of ammonia and hydrazine do not differ very much. Actually, the stability of $N_2H_5ClO_4$ is much lower. It can be assumed that during the decomposition of $N_2H_5ClO_4$ the interaction of N_2H_4 or the complex ion $N_4H_9^+$ with a molecule of perchloric acid occurs with the formation of oxidation products and ammonia. Only in the region of the existence of hydrazinium diperchlorate and with an even greater perchloric acid content does its own thermal decomposition become decisive.

The table gives temperature relationships and values of the first rate constants k_1 at 120, 150, and 200°C for the investigated compounds and recalculation of the literature data for $N_2H_5ClO_4$. The rate curves are satisfied by various kinetic equations because of the difference in the mechanisms of the studied reactions; however, the value of k_1 is always equal to the initial reaction rate and therefore can serve as a characteristic of the stability of this salt.

An increase in the decomposition rate of N_2H_5I basically involves less activation energy of the interaction of hI with N_2H_5I as compared with the thermal decomposition of the complex $N_2H_4 \cdot N_2H_5^+$. A further drop in the activation energy for $N_2H_5N_3$ is caused by the high volatility of HN_3 at elevated temperatures;

the effective activation energy is reduced to the heat of vaporization of HN_3 from the melt, while the preexponent is reduced to a corresponding change in entropy.

Substance	$k_1 = f(T)$, s^{-1}	k_1, s^{-1}		
		120°C	150°C	200°C
$N_2H_5NO_3$	$10^{12.2} e^{\frac{-38000}{RT}}$	$10^{-8.9}$	$10^{-7.4}$	$10^{-5.3}$
N_2H_5Cl	$10^{13.2} e^{\frac{-40000}{RT}}$	$10^{-8.0}$	$10^{-7.4}$	$10^{-5.2}$
N_2H_5I	$10^{13.55} e^{\frac{-35000}{RT}}$	$10^{-6.8}$	$10^{-3.5}$	$10^{-1.7}$
$N_2H_5N_3$	$10^{8.0} e^{\frac{-21000}{RT}}$	$10^{-5.3}$	$10^{-4.4}$	$10^{-3.1}$
$N_2H_5ClO_4$			$10^{-3.55}$	10^{-2}

Changes in the reaction rate during the process are associated with the effect of the products formed. In all cases one of the end products is ammonia which can extract hydrazine from the hydrazinium salts:

$$NH_3 + N_2H_5X \rightleftarrows N_2H_4 + NH_4X. \tag{6}$$

Therefore, at least in the first stages of the reaction, an accumulation of free hydrazine occurs, while it is the end product for $N_2H_5N_3$. When an increase in N_2H_4 concentration leads to an increase in the reaction rate ($N_2H_5NO_3$, N_2H_5Cl, the concentration of the $N_4H_9^+$ complexes increases), the process continues with significant self-acceleration. In N_2H_5I the ammonia and hydrazine decrease the equilibrium concentration of HI and the rate drops during the process; in $N_2H_5N_3$ both possible mechanisms proceed at commensurate rates; a certain time of the orders of the reaction is close to zero, but subsequently, the rate drops with decreasing quantity of the basic substance.

Thus, the thermal decomposition of hydrazinium salts for all the compounds investigated goes through equilibrium dissociation to hydrazine and acid, while the reaction rate is determined by the

decomposition rate of the products of this dissociation; in addition,
at the present time two possible means for such a process have
been established.

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